Non-Faradaic Processes and Tafel Plots

Non-Faradaic Processes (B&F Chapter 1.2.4)

Example Work-Up and Questions

1) Plot the charging curve for the Pt black electrode. Estimate the surface area of the Pt black electrode assuming that charging the double layer of such an electrode in 1 M H_2SO_4 requires $\approx$ 210 μC cm^{-2}.

Figure 1 compares typical charging curves obtained for a Pt black electrode using the set-up in Noyes with the curve included in the lab hand-out. Observing the lab as the class did it, at least once I saw a curve that closely resembled the example, clearly showing the A, B, C, D, E, and F regions (the first time I ran a fresh electrode). But the curve shown was more typical of what happened later. In that case, the electrode never reached the oxygen-evolution portion of the curve (D). Also, the potential for the first current step was much more positive than expected, and so the (A) region was missed. If you clearly saw (A), but not (F), you could estimate the surface area based on the charge passed in (A). If you didn't see those regions, but saw (C), you could estimate from that (although that is associated with oxygen instead of hydrogen). For this example, none of those regions is clear. So, the best we can do is estimate where (F) would be.

The answer in this example is going to be no better than a guess due to the timing of the current steps. For the charge passed in (F), we can guess $Q = -0.1mA \times (50s - 30s) = -2mC$. Then, dividing by 210 μC/cm^2, we get an area of 9.5 cm^2, which is almost certainly wrong (too high). However, it really isn't clear where in that 30-50s window to start measuring (and we don't know where to stop either because at 50 s the current step was ended). Taking the second derivative, it looks like there's an inflection around 35.6 s, but still gives an area (6.8 cm^2) that seems too high. For this example, we would probably want to redo the experiment with some modifications, for example: 1) Hold the electrode at a negative current (hydrogen evolution) for several minutes to clean it before taking measurements (since we were reusing electrodes, and so in most cases the Pt black electrodes had recently been used for the oxygen-evolution part of the Tafel lab, so they could be quite oxidized); 2) Make sure that we hold the current steps long enough to reach the regions where Faradaic current is passed (D,G).

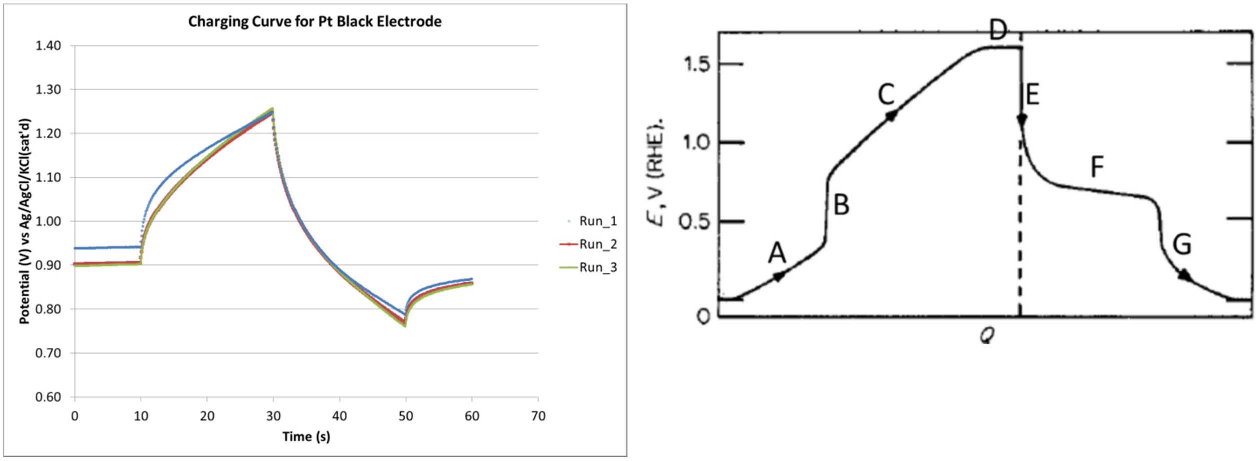

Figure 1. (left) Potential versus time for a 0.1 mA current step (at 10 s) followed by a -0.1 mA current step (at 30 s). (right) Example Pt charging curve from the lab hand-out.

2) Make plots of the E versus t data for the various current steps. For each data set, calculate R_s and C_d. Are the values consistent?

Figure 2 shows an example of plots for 20 μA, 50 μA, and 100 μA current steps. The slopes of the fits lines were: 2.2×10^{-3}V/s for i=20 μA; 5.7×10^{-3}V/s for i=50 μA; and, 3.8×10^{-3}V/s for i=100μA. The intercepts were: 1.17V for i=20 μA; 0.99V for i=50 μA; and, 1.34 V for i=100μA. The slopes yield values of 9.23mF, 8.8 mF, and 26 mF for C_d. The intercepts yield values of 58 kΩ, 20 kΩ, and 13 kΩ for R_s, but I think I should consider the intercept at t=10 (where the step begins), not at t=0, and also should correct for the difference in the starting potentials when i=0. Doing this gives me R_s values of 4.5 kΩ, 2.5kΩ, and 2.4 kΩ. From these results, it looks like C_d is 9 mF, and R_s is a few kΩ.

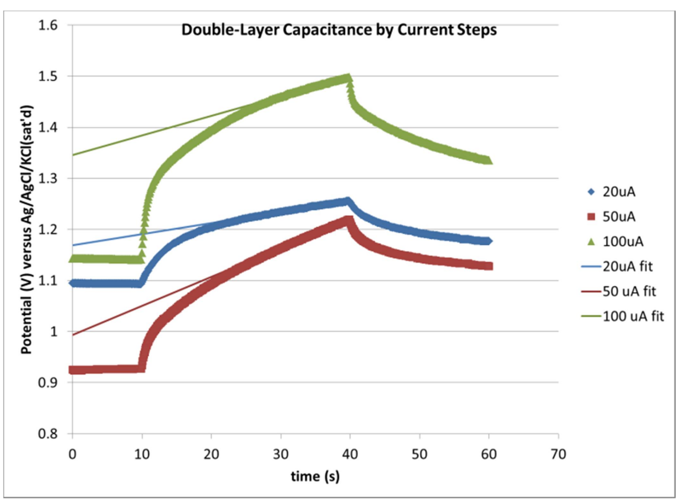

Figure 2. Plots of Potential versus time for current steps of 20, 50, and 100 μA, plus fit lines for each.

3) Make plots of the i versus t data for the various potential sweep rates. For each data set, calculate C_d. Are these values consistent?

Figure 3 shows an example. Note this plot is baseline-corrected to get the first point at zero current. The data from the 50 mV/s sweep looks pretty messed up, so we will ignore it. The data yield currents of 2.95×10^{-4} A, 4.03×10^{-4} A, and 8.47×10^{-4} A for sweep rates of 5, 10, and 20 mV/s respectively. Thus, C_d is calculated as 59 mF, 40 mF, 42 mF, yielding an average value of C_d=47 mF.

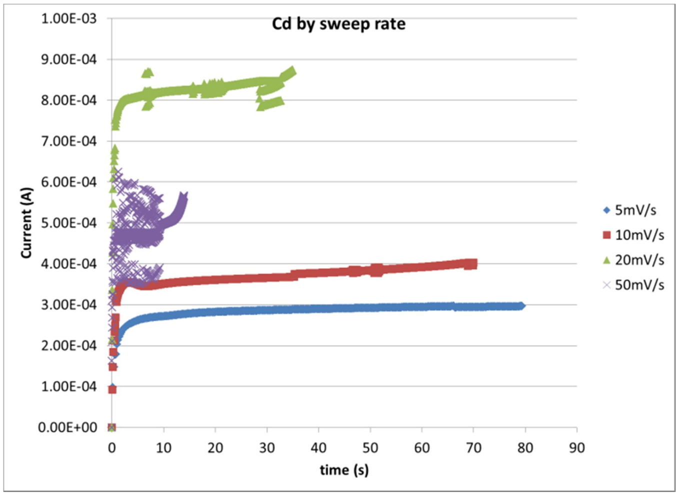

Figure 3. Example of plots of non-Faradaic current versus time for varied sweep rates.

4) Do the values of C_d measured by the two techniques agree?

No, they did not agree, but are off by about a factor of 5 from each other. Since C_d is usually in the range of 10-40 μF/cm^2, values on the order of 10 mF for these electrodes (even if they are 10 cm^2) seem way too high to be correct. Yet the general behavior seems to be correct, i.e., linear plots for the potential steps and leveling off for the sweeps. Most likely the issues are related to the baselines (e.g., $i\neq0$ at $t=0$).

Tafel Plots (B&F 3.4.3)

Work-Up and Questions

1) Make a plot of overpotential versus log(|j|) for H_2 evolution. What is the exchange-current density, j_0? What is the slope of the Tafel plot?
2) Make a plot of overpotential versus log(|j|) for O_2 evolution. What is the exchange-current density, j_0? What is the slope of the Tafel plot?

Figure 4 shows the requested plots for H_2 and O_2 evolution. The exchange currents are found from the intercepts for the plots. For H_2, i_0=7.5 μA; for O_2, i_0=26 μA. Usually, slopes of Tafel plots are given in units of mV per decade. Of course, the slope of the plots below would be in units of decades of current per V. For H_2, the slope is -21 decades per V, (-47 mV per decade); For O_2, the slope is 3.3 decades per V (300 mV per decade).

Of course the H_2 side in this plot is not really linear, so these values are quite sensitive to which points are considered to be part of the linear region for the regression. I think what's going on here is that at high overpotentials we may be hitting mass-transport limits. The example from the lab textbook also shows a rather curved plot for H_2, and a more linear plot for O_2. The literature values for H_2 at a Pt black electrode are on the order of a few tens of mV per decades, with i_0=9.5 μA cm^{-2}. For O_2 at a smooth Pt electrode (not what we used here), the slope is ~120 mV per decade and j_0=0.13 μA cm^{-2}.

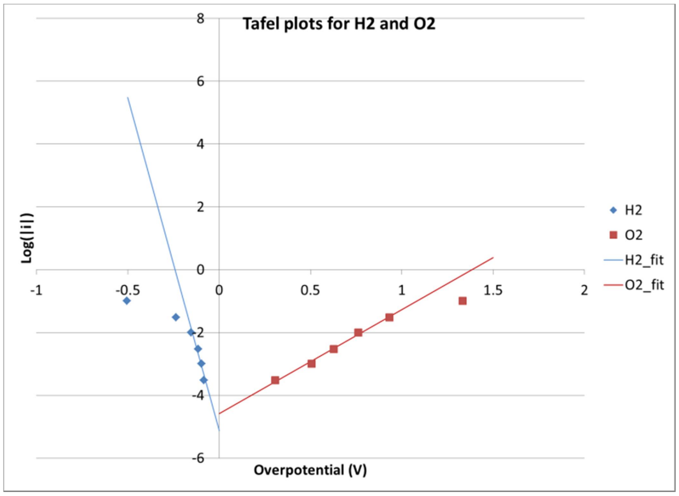

Figure 4. Tafel plots for H_2 and O_2 evolution.